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(71) Applicants
United Technologies
Corporation,
United Technologies
Building,
Hartford,
Connecticut 06101,
United States of America.
(72) Inventors
Conrad Martin Banas,
Duane Louis Ruckle,
Francis Salvatore
Galasso.
(74) Agents
McNeight and Lawrence,
Regent House,
Heaton Lane,
Stockport,
Cheshire SK4 1BS.

(54) Strain tolerant thermal barrier coatings

(57) Methods are described for producing metallic substrates having strain tolerant ceramic coatings thereon. The metallic substrate is provided with an adherent dense ceramic coating. The ceramic coating is then partially melted and allowed to solidify. Cracks develop upon solidification which improve the strain tolerance of the ceramic, and render it resistant to spallation during thermal cycling.

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FIG. 1

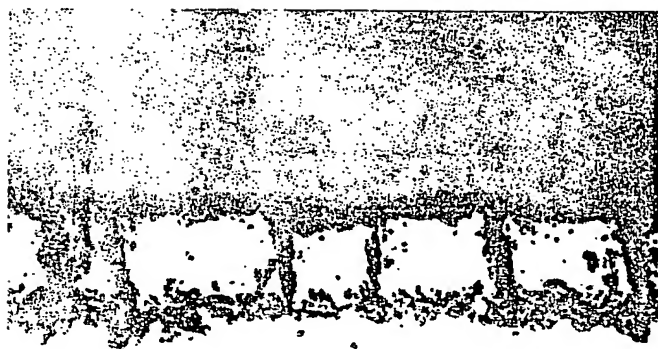
100 X



← melted
← unmelted
ceramic
← substrate

FIG. 2

100 X



SPECIFICATION

Method for providing a strain tolerant ceramic thermal barrier coating on a metallic substrate

5 The present invention concerns a method for providing a strain tolerant ceramic coating on a metal substrate.

10 The art has long sought to combine the properties of ceramics with the properties of metals. Thus for example, many attempts have been made to provide protective ceramic coatings to metal articles which find application at elevated temperatures so as to combine the thermal properties of ceramics with the toughness of metals.

15 The major problem which has not heretofore been successfully solved is that the substantial difference in the coefficient of thermal expansion of metals and ceramics invariably leads to failure of ceramic coatings under conditions of thermal cycling.

20 One approach which has been employed in an effort to overcome this problem is that of grading the coating from essentially all metal at the metal surface to all ceramic at the outer surface of the coating. In this way it is believed that the coefficient of thermal expansion will change gradually through the coating thickness and the stress resulting from thermal cycling will not be sufficient to cause damage to the coating. Such an approach is described in U.S. Patent no. 3 091 548. The problem with the graded approach is that the discrete metal particles in the graded coating oxidize and increase in volume producing unacceptable stresses in the coating.

35 In the general area of metal-ceramic combinations, it is known to use segmented ceramic pieces such as tiles which are bonded to metal structures for their protection. In this approach, which is generally applied to large metallic articles, the segments are not bonded to each other, and the gaps between the tiles permit accommodation of the thermal expansion of the metal. Such an approach (the application of individual segments) would generally not be practical in the case of small components such as gas turbine components in which extreme operating conditions will be encountered and which a multiplicity of small complex parts must be coated at a reasonable cost. Additionally, in the use of such a segmented ceramic approach, there still remains the problems of obtaining a good metal-ceramic bond.

45 The present invention includes a method for producing segmented ceramic coatings on metal substrates as well as the resultant composite articles. The invention presumes that the metallic article has an adherent ceramic coating on its exterior. Preferably, a bond coat or inter-layer is interposed between the substrate and coating to aid adherence. The ceramic surface layer is cracked or segmented through the use of a high intensity heat source. The free surface of the ceramic is rapidly melted and cracking occurs upon solidification.

50 Other features and advantages will be apparent from the specification and claims and from the accompanying drawings which illustrate an embodi-

ment of the invention.

Figure 1 is a photomicrograph showing a cross section of a segmented ceramic coating.

70 *Figure 2* is a photomicrograph showing a cross section of a segmented ceramic coating.

The present invention has a wide spread application. The segmented ceramic coatings of the invention may be applied to substrates of many different materials including those based on iron, nickel and cobalt. In like manner, the ceramic coating may be selected from a wide group of ceramics including zirconia (preferably stabilized with a material such as yttria), alumina, ceria, mullite, zircon, silica, silicon nitride, hafnia and certain zirconates, borides and nitrides.

80 A necessary preliminary to the present invention is the provision of a substrate coated with a dense continuous adherent ceramic coating. To date, plasma spraying has been used to apply the ceramic coating, but it is envisioned that other techniques including slurry coating and sputtering could also be used. The coating must be adherent to the substrate and adherence can best be obtained through the use of an intermediate bond coat. A variety of bond coats are possible including those based on MCr where chromium ranges from about 20 to about 45%, those based on MCrAl where chromium ranges from about 15 to about 45% and aluminium ranges from about 7 to about 15%, those based on MCr, those based on MCrAlY where cobalt ranges from about 15 to 45%, aluminium ranges from about 7 to about 20% and yttrium ranges from about 0.1 to about 5% and those based on MCrAlHf where chromium ranges from about 15 to about 45%, aluminum ranges from about 7 to about 15% and hafnium ranges from about 0.5 to 7%. In all of these bond coats, "M" is selected from the group consisting of nickel, cobalt and iron and mixtures thereof with mixtures of nickel and cobalt being particularly favored. Minor additions of other elements including silicon may be made to all these compositions without adversely affecting their utility as a bond coat, and yttrium may be partially substituted for by one or more rare earth elements. The MCrAlY bond coats are preferred and provide a surprising degree of adherence to ceramic coatings as described in U.S. patent 4 248 940 which is incorporated herein by reference. However, what is important to this invention is that the ceramic coating adhere to the substrate and specific details on how this result is obtained do not form a necessary part of the invention.

100 The bond coat, if used, may be applied by a variety of techniques including physical vapor deposition and plasma spray deposition. Plasma spray deposition is preferred for reasons of economics. Bond coat thickness may range widely, e.g. from 0.025 to 2.54 mm.

105 As previously indicated, the ceramic coating must be dense and in the case of plasma spraying this can be achieved through control of the plasma spray parameters. In general, dense coatings can be obtained through the use of fine ceramic powders whose particle size is limited in range in combination with the use of a higher than normal power input. For the particular case of stabilized zirconia sprayed

using a Plasmadyne SG100 gun, the use of powder which has been sieved to provide 0.044 mm powder with less than 20% of the powder smaller than 0.055 mm and less than 10% of the powder being smaller than 0.037 mm was found to provide good results. In the same situation, a power input of 50 volts and 800 amps was employed and the gun to specimen distance was about 76.2 mm. The deposition was performed in air using an argon - 5% helium carrier gas and the substrate was cooled to less than 316°C. Again, the ceramic coating thickness may vary widely depending upon the intended application. Coating thicknesses of 0.025 mm to 6.35 mm and greater appear useful.

For the purpose of this invention, a dense ceramic coating is one having less than about 15% porosity and preferably less than about 10% porosity as measured by metallographic methods. Specifically in the present invention, the coated articles were sectioned, mounted and polished using polishing techniques which did not result in the pull-out of particles; porosity evaluations were then made using a Quantimet™ apparatus.

Even such apparently dense ceramic coatings as that previously described may fail under conditions of severe thermal cycling unless segmented by the process of the present invention as described below. By segmenting the coating, cracks are provided which permit expansion of the underlying substrate while limiting the compressive stresses in the ceramic coating to a level below that which will cause failure.

The ceramic coatings are segmented by using a high intensity heat source to partially melt the ceramic coating and then allow the melted ceramic to solidify. The contraction which occurs during solidification produces the described segmentation effect. The invention process requires a high intensity heat source. All experimental work to date involves the use of a continuous wave CO₂ laser, but it is anticipated that other heat sources such as electron beam technique apparatus or even open flame such as an oxide hydrogen flame would also be satisfactory. It appears that an energy density of about 1.55×10^3 watts per cm² is required. However, the required conditions may best be defined as that combination of energy density and dwell time which will provide partial melting through the thickness of the ceramic layer without causing melting of the substrate or bond coat. Since the ZrO₂ melts at about 2093°C and the typical substrate and bond coat materials melt at about 1316°C, rapid heat input is necessary to melt the ceramic without melting the substrate. On the other hand, too high an energy density will cause evaporation of the ceramic and substantial evaporation of the ceramic should be avoided because it is wasteful of ceramic material and difficult to control. It is therefore preferred to use conditions which will melt through the thickness of the ceramic to a depth of 10 to 90 percent of the ceramic coating thickness without causing significant vaporization of the ceramic. If the melting is less than about 10 percent of the coating thickness, the desired crack network may not develop fully. If the ceramic is melted more than about 90 percent of its

thickness, the probability of melting the substrate and/or bond coat is high. Once melting has been achieved solidification occurs naturally as a result of heat conduction inward to the substrate and heat loss to the atmosphere. When the ceramic is molten it is in a state of stress equilibrium with the substrate. Upon solidification however, a significant decrease in volume occurs which results in the development of tensile stresses in the solidification portion of the ceramic. These tensile stresses exceed the strength of the ceramic and cracks result. The cracks extend through the solidified portion of the ceramic and may extend further, the cracks form a network and divide the ceramic coating into segments whose typical dimension is 8.25 mm. This network of cracks is what is desired to provide a substantial amount of strain tolerance in the ceramic coatings. The cracks depth is substantially equal to the depth of melting however, due to the brittle nature of ceramic, the cracks will easily grow inward until they reach the substrate or bond coating interface. This growth will occur upon exposure to cyclic stress such as that which may result from thermal cycling either in use, or thermal cycling may be purposefully employed prior to service to cause crack growth.

It has been found in certain situations to be necessary to preheat the coated substrate prior to and during the surface melting step. This preheating of the coated substrate produces an initial stress state which effectively eliminates spallation of the ceramic coating upon surface melting. During the surface melting step the ceramic layer is heated and expands to such a degree prior to actual melting of the ceramic that the coating spalls from the substrate as a result of compressive stresses in the ceramic. By preheating the entire coated article the metal substrates expands at a greater rate than does the ceramic coating thereby placing the coating in an initial tensile condition. Upon the surface melting step, the expansion of the ceramic coating is not sufficient to introduce damaging compressive stress. The preheating step is necessary in circumstances where the metal substrate has substantial cross section area relative to the coating. In cases where thin metal components, such as sheet metal components, are to be coated the preheating step would not be necessary since the coated substrate can flex slightly to relieve stresses. For nickel substrates and zirconia coatings a preheat temperature of at least 427°C appears desirable. There is apparently no maximum preheat temperature aside from the obvious danger of melting the substrate and/or bond coat. A further consideration is that if the substrate is heated to a high temperature the likelihood that surface melting temperature will melt the substrate is increased. A temperature range of 427°C to 982°C appears to be the useable.

The result of the invention process is shown in Figures 1 and 2. Both figures show the cross sectional photo-micrograph of ceramic coated nickel substrates after laser surface melting. The ceramic material comprises zirconia stabilized by the addition of 20 weight percent yttrium and was applied to the substrate by plasma spraying. The initial coating

thickness was about 254 microns. The laser beam was adjusted so that the beam had an elliptical cross section with a major axis of about 66.0 mm and minor axis of 254 microns. The power input was 5 kw. Figure 1 shows the results after the beam was scanned over the surface at a rate of 254 cm per minute. This treatment resulted in the melting of about one half the thickness of the ceramic layer and the desired crack structure. The cracks through the melted portion of the ceramic. This result may be seen in the melted portion of the ceramic. Figure 2 shows the result of the treatment that was identical of that of Figure 1 except the rate of beam traverse was reduced to 127 cm per minute. This resulted in a substantial increase in melt depth and again the cracks can be seen to extend to the depth of the melted portion.

As previously indicated, the cracks formed by surface melting can be caused to grow further into the ceramic coating by thermal cycling. For example, heating the cracked coated substrate to a temperature of 538°C and then quenching it in water will cause the cracks to grow toward the substrate or bond coat.

The cracked coating of the invention will find many uses and shows particular promise for use as a thermal barrier coating to protect superalloy components in gas turbine engines. As previously indicated existing plasma spray coatings are sufficient in such applications, however the present technique can expand the range of application for ceramic coatings. It is envisioned that present technique need not be applied over the entire article surface but may be restricted to certain areas where extreme thermal conditions are anticipated.

It should be understood that the invention is not limited to the particular embodiments shown and described herein, but that various changes and modifications may be made without departing from the scope of this novel concept as defined by the following claims.

CLAIMS

1. A method for providing a strain tolerant ceramic thermal barrier coating on a metallic substrate characterized in including the steps of:
 - a. applying a dense adherent ceramic coating to the substrate surface;
 - b. heating the surface of the ceramic coating under conditions which produce surface melting of the ceramic without significant vaporization of the ceramic and without melting the metallic substrate;
 - c. allowing the melted ceramic to solidify; whereby upon solidification of the melted ceramic a network of cracks results in that portion of the ceramic which has been melted, with said cracks being oriented substantially perpendicular to the surface of the ceramic.
2. A method according to claim 1 characterized in that the coated substrate is preheated to a temperature between about 427°C-982°C before the ceramic coating is partially melted.
3. A method for providing a strain tolerant ceramic thermal barrier coating on a metallic sub-

trate characterized in including the steps of:

- a. applying a dense adherent ceramic coating to the substrate surface;
 - b. heating the surface of the ceramic coating under conditions which produce surface melting of the ceramic without significant vaporization of the ceramic and without melting the metallic substrate;
 - c. allowing the melted ceramic to solidify;
 - d. cyclically heating and cooling the partially cracked coated substrate;
- whereby upon solidification of the melted ceramic a network of cracks results in that portion of the ceramic which has been melted, with said cracks being oriented substantially perpendicular to the surface of the ceramic; and whereby upon cyclic heating and cooling the cracks propagate inward toward the substrate.
4. A method according to claim 3, characterized in that the coated substrate is preheated to a temperature between about 427°C-982°C before the ceramic coating is partially melted.
 5. A method for providing a strain tolerant ceramic thermal barrier coating on a metallic substrate characterized in including the steps of:
 - a. applying a metallic bond coat to the substrate surface;
 - b. applying a dense adherent ceramic coating to the bond coat surface;
 - c. heating the surface of the ceramic coating under conditions which produce surface melting of the ceramic without significant vaporization of the ceramic and without melting the metallic substrate;
 - d. allowing the melted ceramic to solidify; whereby upon solidification of the melted ceramic a network of cracks results in that portion of the ceramic which has been melted, with said cracks being oriented substantially perpendicular to the surface of the ceramic.
 6. A method according to claim 5, characterized in that the coated substrate is preheated to a temperature between about 427°C-982°C before the ceramic coating is partially melted.
 7. A method for providing a strain tolerant ceramic thermal barrier coating on a metallic substrate characterized in including the steps of:
 - a. applying a metallic bond coat to the surface of the substrate;
 - b. applying a dense adherent ceramic coating to the bond coat surface;
 - c. heating the surface of the ceramic coating under conditions which produce surface melting of the ceramic without significant vaporization of the ceramic and without melting the metallic substrate;
 - d. allowing the melted ceramic to solidify;
 - e. cyclically heating and cooling and partially cracked coated substrate;

whereby upon solidification of the melted ceramic a network of cracks results in that portion of the ceramic which has been melted, with said cracks being oriented substantially perpendicular to the surface of the ceramic and whereby upon cyclic heating and cooling the cracks propagate inward, toward the substrate.
 8. A method according to claim 7 characterized in that the coated substrate is preheated to a

temperature between about 427°C-982°C before the ceramic coating is partially melted.

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